(54) A METHOD FOR INHIBITING THE PLUGGING OF CONDUITS BY GAS HYDRATES

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PROCEDE DESTINE A EMPECHER L'OBSTRUCTION DE CONDUITS PAR DES HYDRATES DE GAZ

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Description

This invention relates to a method for inhibiting the plugging by gas hydrates of conduits containing a mixture of low-boiling hydrocarbons and water.

5   Gas hydrates are clathrates (inclusion compounds) of gases in a lattice consisting of water molecules.

Low-boiling hydrocarbons, such as methane, ethane, propane, butane and iso-butane, are present in natural gas and also in crude oil. Because water may also be present in varying amounts in natural gas and crude oil, the mixture, under conditions of elevated pressure and reduced temperature, tends to form gas hydrate crystals. The maximum temperature at which gas hydrates can be formed strongly depends on the pressure of the system. For example,

10   ethane at a pressure of approximately 1MPa can form hydrates only at temperatures below 4 °C whereas at a pressure of 3MPa stable hydrates can be present at temperatures as high as 14 °C. With respect to this strong dependence of the hydrate melting point on pressure, hydrates markedly differ from ice. As described by M. von Stackelberg and H. R. Muller (Z. Electrochem. 1954 58 25), methane and ethane hydrates form cubic lattices having a lattice constant of 1.2 nm (hydrate structure I). The lattice constant of the cubic propane and butane gas hydrates is 1.73 nm (hydrate

15   structure II). However, the presence of even small amounts of propane in a mixture of low-boiling hydrocarbons will result in the formation of gas hydrates having structure II (J. H. van dor Waals and J. C. Platteeuw, Adv. Chem. Phys. 2 1959 1).

It has been known for a long time, that gas hydrate crystals, when allowed to form and grow inside a conduit such as a pipeline, tend to block or even damage the conduit. To prevent such blocking, the following thermodynamic meas-

20   ures are possible in principle: removal of free water, maintaining elevated temperatures and/or reduced pressures or the addition of melting point depressants (antifreeze). In practice, the last-mentioned measure is most frequently applied. However, the antifreeze, such as the lower alcohols and glycols, have to be added in substantial amounts (several tens of percent by weight of the water present) to be effective. An additional disadvantage of such amounts is that recovery of the antifreezes is usually required during further processing of the mixture.

25   An attractive alternative to the anti-hydrate measures described above, particularly the antifreezes, is to use a crystal growth inhibitor. The principle of interfering with crystal growth is known.

Plants and poikilothermic animals such as insects and cold-water fish are known to protect themselves from freezing, both by antifreezes such as glycols and by special peptides and glycopeptides (termed Antifreeze Proteins, AFP's and Antifreeze Glycoproteins, AFGP's) which interfere with ice crystal growth (A. L. de Vries, Comp. Biochem. Physiol,

30   73 1982 627). The present applicants found such cold-water fish peptides and glycopeptides also to be effective in interfering with the growth of gas-hydrate crystals. However, their production and use for this purpose are currently considered to be uneconomical.

European patent application 309210 discloses the use of certain surface active agents, such as phosphonates, phosphonic acids, phosphate esters and acrylic polymers, for inhibiting the growth of gas hydrate crystals in conduits.
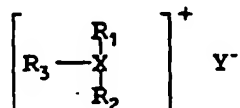
35   In International patent application No. PCT/EP93/01519 the use of polymers and copolymers of N-vinyl-2-pyrrolidone for inhibiting the formation, growth and/or agglomeration of gas hydrate crystals is disclosed.

It is therefore an object of the present invention to provide a method to inhibit formation of hydrates in streams containing at least some light hydrocarbons and water. It is a further object to provide such a method wherein a high concentration of additive is not required.

40   It has now been found that certain alkylated ammonium, phosphonium or sulphonium compounds are very effective, in relatively low concentrations, in interfering with the growth of gas hydrate crystals, and therefore that they can be very useful in inhibiting the plugging by gas hydrates of conduits containing low-boiling hydrocarbons and water. The subject compounds have three or four alkyl groups in their molecule, at least three of which are independently chosen from the group of normal or branched alkyls having four to six carbon atoms.

45   These and other objects are therefore accomplished by a method for inhibiting the plugging of a conduit, the conduit containing a flowing mixture comprising an amount of hydrocarbons having from one to five carbons and an amount of water wherein the amounts of hydrocarbons and water could form hydrates at conduit temperatures and pressures, the method comprising the steps of:

50   adding to the mixture an amount of a hydrate formation inhibitor component of the formula

55

$$\left[R_3 - \underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{X}} \right]^+ \quad Y^-$$

wherein R_1, R_2, and R_3 are independently chosen from the group consisting of normal and branched alkyls having at least 4 carbon atoms,

X is selected from the group consisting of S, N-R_4, and P-R_4,

R_4 is selected from the group consisting of hydrogen and organic substituents and

Y⁻ is an anion, the amount effective to inhibit formation of hydrates in the mixture at conduit temperatures and pressures; and

flowing the mixture containing the hydrate formation inhibitor through the conduit.

Ammonium (X is N-R_4) and phosphonium (X is P-R_4) alkylated compounds according to the invention are preferred. As indicated above, R_4 can be very broadly chosen. R_4 may also contain one or more heteroatoms, such as oxygen. More in particular R_4 can be chosen from the group of alkyls, alkenyls, aryls, arylalkyls, arylalkenyls, alkylaryls, alkenylaryls and glycols having from 1 to 20 carbon atoms.

Preferred are ammonium or phosphonium alkylated compounds according to the invention wherein R_4 is an alkyl or alkenyl group having from 8 to 20 carbon atoms.

The alkylated compounds according to the invention can be chemically bound through their R_4 group to polymers. They then are branches of these polymers. Examples of polymers to which the alkylated compounds according to the invention can be suitably bound are polyacrylic acid, and polymers and copolymers of N-vinyl-2-pyrrolidone.

R_1, R_2 and R_3 of the alkylated compounds according to the invention are preferably independently chosen from the group of n-butyl, iso-pentyl and n-pentyl.

Particularly preferred cations of the alkylated compounds of the invention are those of tributyldecylammonium, tripentyldecylammonium, tributylhexadecylammonium and tributylhexadecylphosphonium.

Further features, objects and advantages of the invention will become more readily apparent from the appended claims and from the following detailed description when taken in conjuction with the accompanying drawings, in which

Figs. 1A, 1B and 1C are schematic drawings of the apparatus used to perform Example 1.

Fig. 2 is a schematic drawing of the apparatus used to perform Example 3.

Fig. 3 is a schematic drawing of the apparatus used to perform Example 4.

The anions of the alkylated compounds according to the invention can be broadly chosen. Preferred anions are the hydroxide, carboxylates, halides, sulphates and organic sulphonates.

In the case of the ammonium or phosphonium alkylated compounds according to the invention having three alkyl groups as defined hereinabove, the fourth group attached to the nitrogen or phosphorus atom can be broadly varied without significantly altering the hydrate growth inhibiting properties of these compounds, whereby additional advantages can be achieved by the fourth group. Examples of such fourth groups are long alkyl or alkenyl chains, in particular oleyl, or groups attached to polymers. Exemplary of such polymers wherein the subject compounds can be incorporated by their fourth group are polyacrylic acid, and the polymers and copolymers of N-vinyl-2-pyrrolidone.

When the fourth group R_4 of an alkylated compound according to the present invention is a longer alkyl or alkenyl chain (e.g. one containing more than 12 carbon atoms), its surface-active properties may give the subject compound, in addition to its inherent hydrate crystal growth-inhibiting properties, the following very important additional advantages:

- Emulsify the aqueous into the hydrocarbon phase (W/O emulsion), thereby keeping the concentration of water available for hydrate forming at the conduit wall small.
- Concentrate the subject compound near the water-hydrocarbon interfaces, where hydrate formation is most pronounced, thereby raising the local concentration of ions to freezing-point depressing level.
- Modify the structure of water near the hydrocarbon-water interface in such a way that the formation of hydrate crystals is hindered.
- Impede further access of water molecules to the hydrate crystal after attachment of the subject compound to the hydrate crystals.
- Prevent agglomeration of hydrate crystals by making their surface hydrophobic.
- Adhere the subject compound to the conduit wall, thereby preventing the adhesion of hydrates thereto.

The amount of the alkylated compounds used in the process according to the invention is generally between 0.05 and 5 wt%, preferably between 0.1 and 0.5 wt%, based on the amount of water in the hydrocarbon-containing mixture.

It will be understood that the compounds used have to be soluble in water at the concentration required and at a temperature of about 5 °C.

The alkylated compounds according to the invention can be prepared in manners which are known in the art, from ingredients which are simple and abundantly available.

The alkylated compounds according to the invention can be added to the subject mixture of low-boiling hydrocarbons and water as their dry powder or, preferably, in concentrated solution.

The alkylated compounds according to the present invention can be used together with the polymers and copol-

ymers of N-vinyl-2-pyrrolidone which are the subject of the aforementioned International patent application No. PCT/ EP93/01519 and the combined effect is at least additive. The latter are preferably added to an amount of between 0.05 and 4 wt%, based on the water content.

The following Examples will illustrate the invention.

Example 1

In this screening example, an aqueous solution of tetrahydrofurane (THF) was used as a model for wet gas, since tetrahydrofurane in water is known to form hydrate (structure II) crystals at about the same temperature as wet gas, but already at atmospheric pressure - for example, an 18.9 wt% aqueous solution of THF has a hydrate melting point of 4.3 C at atmospheric pressure.

The effect of different additives on the growth of a single hydrate crystal was studied by adding 0.5 wt% (based on the total amount of liquid) of an additive to a solution of 18.9 wt% THF in water (approx. molar ratio 1:17), also containing 3 wt% of NaCl, and performing the experiments described below.

A glass vessel, open to atmospheric pressure and containing the solution to be tested is immersed in a thermo-statically controlled bath. After thermal equilibrium has been reached, a capillary holding a small ice crystal (about 0.1 gram) is introduced into the solution. In the reference solution, not containing the additives according to the invention, this introduction of a small ice crystal needs the growth of large type II hydrate crystals which are easy to inspect visually. The morphology and weight of the hydrate crystals formed during the 180 minutes at 0 °C after the introduction of the capillary into the different solutions are determined and compared.

It was observed, that under the above experimental conditions hydrate crystals grown in the reference solution (not containing additives) had a distinct and regular appearance. At the beginning of crystal growth geometrically perfect hexagonal plates were frequently observed, while at later stages the crystals acquired pyramidal shapes, the angles between the faces of the pyramids being 70.9 (+/- 1.9) degrees. In all cases flat crystal planes intersected in sharp angles.

By contrast, the addition of 0.5 wt% of several of the ammonium or phosphonium salts mentioned hereafter, resulted under the above experimental conditions in the growth of severely deformed and much smaller hydrate crystals. Addition of the most active of these salts resulted in the formation of crystals having the appearance of a sheet of paper crushed into a ball, whereas other salts induced the formation of hydrate crystals exhibiting rounded edges between the crystal planes, sometimes to such an extent that flat crystal faces were barely visible.

The experimental set-up is shown schematically in Fig. 1A, Fig. 1B, and Fig. 1C, wherein 11 is the thermostatically controlled bath, 12 the solution to be tested, 13 the capillary, 14 the ice crystal seed, 15 a hydrate crystal grown in the THF/NaCl solution without additive and 16 a hydrate crystal grown in the THF/NaCl solution containing an effective additive.

Table 1 presents the results of a series of experiments 1.1-1.41, whereby 0.5 wt% of additives according to the invention were added, and comparative experiments 1.42 - 1.44. After 180 minutes at 0 °C, the crystals were weighed and their general appearance was classified as follows:

RP = Regular Pyramids
CS = Crumbled Sheet
RE = Rounded Edges

TABLE 1

Ex.	Appearance	Crystals	
		Weight	Appearance
1.1	tetrapentylammoniumbromide	< 0.1 grams	CS
1.2	tripentylbutylammoniumbromide	< 0.1 grams	CS
1.3	triisopentybutylammoniumbromide	< 0.1 grams	CS
1.4	triisopentylammoniumsulphate	0.1 grams	RE
1.5	tetrabutylphosphoniumchloride	0.1 grams	RE
1.6	tributyldecylammoniumbromide	0.4 grams	RE
1.7	tributylisopentylammoniumbromide	0.6 grams	RE

TABLE 1   (continued)

Ex.	Appearance	Crystals	
		Weight	Appearance
1.8	tripentylammoniumsulphate	0.8 grams	RP
1.9	tributyltetradecylammoniumbromide I	0.8 grams	RE
1.10	tributylpentylammoniumbromide	0.9 grams	RP
1.11	tributyltetradecylammoniumbromide II	1.0 grams	RE
1.12	tetrabutylammoniumbromide	1.1 grams	RE
1.13	tetrabutylammoniumchloride	1.2 grams	RE
1.14	tributyltetradecylammoniumbromide III	1.4 grams	RE
1.15	tributylhexadecylphosphoniumbromide	1.7 grams	CS
1.16	tetrabutylammonium-toluene-4-sulfonate	1.9 grams	RE
1.17	tributylammoniumsulphate	2.2 grams	RP
1.18	trihexylbutylammoniumbromide	2.3 grams	RP
1.19	dibutypentylethanolammoniumbromide	2.4 grams	RP
1.20	tributylheptylammoniumbromide	2.6 grams	RP
1.21	tetrahexylammoniumbenzonate	3.8 grams	RP
1.22	tetrahexylammoniumbromide	4.4 grams	RP
1.23	tributylmethylammoniumbromide	4.7 grams	RP
1.24	dibutyldodecylethanolammoniumbromide	4.9 grams	CS
1.25	tetrahexylammoniumchloride	5.7 grams	RP
1.26	triisobutylpentylammoniumbromide	7.0 grams	RP
1.27	(3-dimethylaminopropyl) triphenylphosphoniumbromide	7.0 grams	RP
1.28	dipentylammoniumsulphate	7.4 grams	RP
1.29	tetramethylammoniumbromide	7.4 grams	RP
1.30	methyltriphenylphosphoniumbromide	8.0 grams	RP
1.31	tetradecyltrimethylammoniumbromide	9.9 grams	RP
1.32	butyltriphenylphosphoniumbromide	10.4 grams	RP
1.33	tetrapropylammoniumbromide	10.7 grams	RP
1.34	propyltriphenylphosphoniumbromide	11.6 grams	RP
1.35	tetraphenylphosphoniumbromide	12.0 grams	RP
1.36	tetraethylammoniumbromide	12.1 grams	RP
1.37	dodecyltrimethylammoniumbromide	12.3 grams	RP
1.38	2-dimethylaminoethyl-triphenyl phosphoniumbromide	13.9 grams	RP
1.39	ethyltriphenylphosphoniumbromide	14.0 grams	RP
1.40	ethylhexadecyldimethylammoniumbromide	15.9 grams	RP
1.41	octadecyltrimethylammoniumbromide	17.4 grams	RP
1.42	no additive I	12.3 grams	RP
1.43	no additive II	13.2 grams	RP
1.44	no additive III	14.2 grams	RP

In the above results, the additives resulting in crystals having a weight of less than 3.0 grams and having a "crumbled sheet" (CS) appearance or "rounded edges" (RE) were considered to be particularly effective. From the results of Example 1, it can be seen that experiments 1.36 through 1.41 compounds were tested that did not have alkyl groups within the scope of the present invention, and these in particular resulted in crystals of a weight similar to experiments 1.42 through 1.44 in which no additive was used.

Example 2

Field flow conditions were simulated in an experimental set-up as schematically shown in Fig. 2, comprising a two-litre stirred high-pressure autoclave (21) connected via a gear pump (22) to a coiled copper pipeline (23) of 16 m length and 6 mm internal diameter which is immersed in a thermostatically controlled bath (24). The pressure difference between the inlet and outlet of the pipeline is continuously monitored by a differential pressure transmitter (25).

The autoclave was loaded at 13 °C with 400 ml of synthetic sea water (composed of 24.66 g NaCl, 11.33 g MgCl$_2$, 6H$_2$O, 4.16 g Na$_2$SO$_4$, 1.13 g CaCl$_2$, 0.78 g KCl and 0.09 g NaBr per litre of demineralized water) and with 800 ml of a typical gas condensate having the following composition:

0.02 mol% propane
2.41 mol% iso-butane
9.92 mol% n-butane
7.70 mol% iso-pentane
7.58 mol% n-pentane
14.07 mol% n-hexane
14.60 mol% fraction boiling between 70-100°C (major components methycyclopentane, benzene, cyclohexane, n-heptane, methylcyclohexene, toluene, and ethylcyclopentane)
22.45 mol% fraction boiling between 100-150°C (major components n-heptane, methlcyclohexane, toluene, ethylcyclohexane, octane, ethylbenzene, propylcyclohexane, xylene (P, M, O), nonane, decane, propylbenzene)
11.74 mol% fraction boiling between 150-215 °C (major components include decane and undecane)
9.54 mol% fraction boiling above 215 °C.

In addition, the autoclave was loaded with ethane until the pressure (at the starting temperature, 13 °C) within the autoclave was 2 MPa. After loading and closing the autoclave, the stirred mixture was circulated through the system at a rate of 6.1 litres/hour. The temperature of the bath was lowered gradually, at a rate of 5 °C per hour, either until the pressure drop between the inlet and outlet of the coiled pipeline exceeded 0.1 MPa (at which stage the loop was considered to be blocked and the experiment terminated) or down to a pre-set minimum temperature of 0.5 °C or minus 1 °C. If the loop did not block during the cooling stage, the circulation of the mixture was continued at the pre-set minimum value until plugging occurred. To initiate the formation of hydrates, a piece of dry ice (solid CO$_2$) was held against the inlet of the coiled pipeline. During the gradual cooling stage the pressure drop over the coiled pipeline and the temperature of the bath were continuously monitored as a function of time.

Without any additive, the pressure over the loop gradually increased until the pipeline blocked when the temperature of the bath reached 6 °C.

When 0.5 wt% of the additive tributyltetradecylammoniumbromide was added to the condensate-water mixture, the pipe reached the pre-set minimum temperature of 0.5 °C after which the mixture was circulated for another five hours before the pipeline suddenly blocked.

When 0.25 wt% tetrapentylammoniumbromide and 0.25 wt% "GAFFIX" is added to the condensate-water mixture, the loop reached the pre-set temperature of -1 °C, after which the mixture circulated for another 9 hours before the pipeline blocked. Again, no steady increase of the pressure drop was observed prior to blockage.

Example 3

The experimental set-up was as in Example 2, except that 200 ml of a 7 wt% aqueous solution of NaCl was used instead of 400 ml of synthetic sea water.

Without any additives, the pressure drop over the pipeline gradually increased until the loop blocked when a temperature of 4.2 °C was reached.

When 0.5 wt% of tributylehexadecylphosphoniumbromide is added to the 200 ml of water containing the 7 wt% of sodium chloride, the loop reached the pre-set temperature of -2 °C, after which the mixture was circulated for another 50 hours before the pipeline blocked.

Example 4

In this example, field conditions were simulated by using equipment as is shown schematically in Fig. 3. The set-up comprises a mixing tank (31), a stainless steel pipeloop having an inner diameter of 19 mm (32a-c), and a gear
5   pump (33) for circulating a hydrate forming mixture of water and liquid hydrocarbons through the loop.

The part of the loop in which the formation and transport of gas hydrates under conditions of turbulent flow is studied is divided in three sections: The first section (32a) has a length of 72 meters and is surrounded by a coaxial pipe through which a temperature-controlled liquid is circulated in a direction opposite to that of the flowing hydrate forming mixture. The second section (32b) has a length of 24 meters and is thermally insulated. The last section (32c)
10 has a length of 12 meters and is also surrounded by a coaxial pipe through which a temperature-controlled liquid is circulated in counterflow to the hydrate forming medium. The pressure drop over 9 consecutive parts of the pipeloop, each having a length of 12 meters, is measured by means of differential pressure meters. Thermometers are placed · at intervals of 12 meters to monitor the temperature of the hydrate forming medium along the loop. Finally, two viewing windows (34a and 34b) are mounted near the inlet and outlet of the second section (32b) to allow visual observation
15 of the hydrate forming mixture.

For each experiment the instrument was loaded with a hydrate forming medium, consisting of 5 litres of water, 7.6 kilograms of ethane and 50 litres of "SHELLSOL D60" (trade name for a mixture of paraffinic and naphthenic hydrocarbons, mainly in the C_{10}-C_{12} range, available from Shell Oil Company, Houston, Texas).

Prior to the start-up of the experiment, the hydrate forming medium was circulated through the loop at a rate of
20 510 litres per hour. During this period the temperature of the liquids flowing through the coaxial pipes surrounding the first and third sections was continuously adjusted until the temperature of the hydrate forming medium was, at every point along the loop, 16 °C. The pressure drop over the length of the pipe at this pre-experimental steady state was 25 kPa.

In the actual experiment the temperature of the liquid surrounding the first section (32a) was lowered continuously
25 so as to cause the temperature T1 of the hydrate forming medium at the end of the second section (32b) to be lowered by 1.0 °C per hour. Simultaneously the temperature of liquid surrounding the third section (32a) was increased to ensure that the hydrate forming mixture re-enters the first section at a constant temperature of 16 °C. In this mode of operation the temperature of the hydrate forming medium rapidly drops over the first 36 meters of the loop after which it becomes practically constant and identical to T1 for another 60 meters before it rises to 16 °C in the last section.
30 Hydrate formation was triggered by cooling 1 cm^2 of the inner surface of the first section, halfway its length, to a constant temperature of -15 °C.

In a control experiment 3.1. the hydrate forming mixture of water/ethane/"SHELLSOL D60" as described above, without further additives, was fed to the apparatus.

In further experiments 3.2., 3.3 and 3.4, not according to this invention, there were respectively added to the hydrate
35 forming medium, based on the water, 7 wt% of sodium chloride and 0.1 or 0.2 wt% of "GAFFIX (COPOLYMER VC-713", a terpolymer of N-vinylpyrrolidone, N-vinylcaprolactam and dimethylaminoethyl- methacrylic acid marketed by ISP CORPORATION, Wayne, NJ, USA.

In yet further experiments, 3.5. - 3.12., one or two of three alkylated compounds according to the invention was added to the hydrate forming medium, with and without concurrent addition of sodium chloride or "GAFFIX".
40 The alkylated compounds tested were tetrapentylammoniumbromide (TPAB), tributylhexadecylphosphonium-bromide (TBHPB) and tributyldecyammonium-bromide (TBDAB).

In all experiments, the temperature at which there occurred an increase of 0.01 kPa in the pressure drop over the length of the pipe, and the temperature at which the flow in the pipe stopped entirely, (blocking temperature) were noted. When no pressure drop could be noted, the system was cooled down to a pre-set temperature of 1 °C (Ex. 9),
45 minus 1 °C (Ex. 10), minus 3.5 °C (Ex. 11) and 0 °C (Ex. 12), and circulation maintained for a maximum of 11, 100, 125 and 70 hours respectively.

The results are presented in Table 2.

TABLE 2

Exp. nbr.	Additives and Concentrations (wt% based on water)	Temperature at which pressure drop starts to increase (Deg. C)	Blocking temperature (Deg. C)
3.1.	no additives	8.3	7.3
3.2.	7.0% NaCl	6.4	5.4
3.3.	0.1% "GAFFIX"	6.0	4.4

TABLE 2 (continued)

Exp. nbr.	Additives and Concentrations (wt% based on water)	Temperature at which pressure drop starts to increase (Deg. C)	Blocking temperature (Deg. C)
3.4.	0.2 "GAFFIX"	4.6	3.2
3.5.	0.1% TPAB	8.3	7.3 .
3.6.	0.2% TPAB	8.5	7.9·
3.7.	0.1% "GAFFIX" & 0.1% TPAB	3.7	2.2
3.8.	0.1% "GAFFIX" % 0.2% TPAB	3.9	2.4
3.9.	0.2% "GAFFIX" & 0.2% TPAB	< 1.0[1]	< 1.0[1]
3.10.	7.0% NaCl & 0.45% TBHPB	< -1.0[2]	< -1.0[2]
3.11.	7.0% NaCl & 0.45% TBHPB	< -3.5[3]	< -3.5[3]
3.12.	0.1% TBHPB 0.3% TBDAB	0.0[4]	0.0[4]

[1]
   In experiment 3.9. the loop was cooled at a rate of 1 °C per hour until a temperature of 1.0 °C was reached. Thereafter the loop was maintained at this temperature for another 11 hours. Then the experiment was terminated without any increase in pressure drop having been observed.
[2]
   In experiment 3.10. the loop was cooled at a rate of 1 °C per hour until a temperature of minus 1 °C was reached. Thereafter the loop was maintained at this temperature for another 100 hours. Then the experiment was terminated without any increase in pressure drop having been observed.
[3]
   In experiment 3.11. the loop was cooled at a rate of 1 °C per hour until a temperature of minus 3.5 °C was reached. Thereafter the loop was maintained at this temperature for another 125 hours during which a slight increase in the pressure drop over the loop was observed. Next, the circulation of the loop contents was stopped during a period of 125 hours whilst the temperature was kept constant at -3.5 °C. Thereafter, a restart appeared to be possible without any additional increase of pressure drop.
[4]
   In experiment 3.12. the loop was cooled at a rate of 1 °C per hour until a temperature of 0 °C was reached. Thereafter the loop was maintained at this temperature for 70 hours after which the pipeline blocked.

Experiments 3.5 and 3.6 did not demonstrate an improvement over the no-additive base case, experiment 3.1, because the additives were not present in a sufficient concentration. Experiments 3.7 through 3.12 are all within the scope of the present invention.

Claims

1. A method for inhibiting the plugging of a conduit, the conduit containing a flowing mixture comprising an amount of hydrocarbons having from one to five carbons and an amount of water wherein the amounts of hydrocarbons and water could form hydrates at conduit temperatures and pressures, the method comprising the steps of:

adding to the mixture an amount of a hydrate formation inhibitor component of the formula
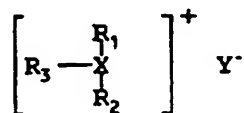
$$\left[R_3 - \overset{R_1}{\underset{R_2}{X}} \right]^+ \quad Y^-$$

wherein R_1, R_2, and R_3 are independently chosen from the group consisting of normal and branched alkyls

having at least 4 carbon atoms,

X is selected from the group consisting of S, N-R_4, and P-R_4,

R_4 is selected from the group consisting of hydrogen and organic substituents and

Y^- is an anion, the amount effective to inhibit formation of hydrates in the mixture at conduit temperatures and pressures; and

flowing the mixture containing the hydrate formation inhibitor through the conduit.

2. The method of claim 1 wherein X is N-R_4.

3. The method of claim 1 wherein X is P-R_4.

4. The method of claim 1 wherein R_1, R_2, and R_3 each have from 4 to 6 carbon atoms.

5. The method of claim 1 wherein R_4 is selected from the group consisting of alkyls, alkenyls, aryls, arylalkyls, arylalkenyls, alkylaryls, alkenylaryls and glycols.

6. The method of claim 5 wherein R_4 is an alkyl having from eight to twenty carbon atoms.

7. The method of claim 6 wherein R_4 is oleyl.

8. The method of claim 5 wherein R_4 is an alkenyl having from eight to twenty carbon atoms.

9. The method of claim 5 wherein the R_4 comprises from one to twenty carbon atoms.

10. The method of claim 1 wherein the R_4 groups link the hydrate formation inhibitor to a polymer.

11. The method of claim 10 wherein the polymer is a polyacrylic acid.

12. The method of claim 1 wherein R_1, R_2, and R_3 are each independently chosen from the group consisting of n-butyl, iso-pentyl and n-pentyl.

13. The method of claim 12 wherein the hydrate formation inhibitor cation is selected from the group consisting of tributyldecylammonium, tripentyldecylammonium, tributyloleylammonium, tributylhexadecylammonium, tributylhexadecylphosphonium and tributyloleylphosphonium.

14. The method of claim 1 wherein Y is selected from the group consisting of hydroxide, carboxylate, halide, sulphate, and organic sulphonate.

15. The method of claim 1 wherein the amount of the hydrate formation inhibitor is between 0.05 and 5 percent by weight based on the water in the mixture.

16. The method of claim 15 wherein the amount of the hydrate formation inhibitor is between about 0.1 and 0.5 percent by weight of the water in the mixture.

17. The method of claim 2 wherein R_1, R_2, and R_3 are each independently chosen from the group consisting of n-butyl, iso-pentyl and n-pentyl.

Patentansprüche

1. Verfahren zum Inhibieren des Verstopfens einer Leitung, welche Leitung ein strömendes Gemisch mit einem Gehalt an einer Menge von Kohlenwasserstoffen mit ein bis fünf Kohlenstoffatomen und an einer Menge Wasser enthält, worin die Mengen an Kohlenwasserstoffen und Wasser bei Leitungstemperaturen und -drücken Hydrate ausbilden könnten, welches Verfahren die folgenden Stufen umfaßt:

Zusetzen einer Menge einer Hydratbildungsinhibitorkomponente der Formel

$$\left[R_3 - \begin{array}{c} R_1 \\ | \\ X \\ | \\ R_2 \end{array} \cdot \right]^+ \quad Y^-$$
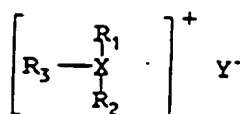
worin R_1, R_2 und R_3 unabhängig aus der aus normalen und verzweigten Alkylen mit wenigstens 4 Kohlen-
stoffatomen bestehenden Gruppe ausgewählt sind,
X aus der aus S, N-R_4 und P-R_4 bestehenden Gruppe ausgewählt ist,
R_4 aus der aus Wasserstoff und organischen Substituenten bestehenden Gruppe ausgewählt ist und
Y^- ein Anion ist und die Menge zum Inhibieren der Ausbildung von Hydraten in dem Gemisch bei Leitungs-
temperaturen und -drücken wirksam ist; und
Strömenlassen des Gemisches, das den Hydratbildungsinhibitor enthält, durch die Leitung.

2. Verfahren nach Anspruch 1, worin X für N-R_4 steht.

3. Verfahren nach Anspruch 1, worin X für P-R_4 steht.

4. Verfahren nach Anspruch 1, worin R_1, R_2 und R_3 jeweils 4 bis 6 Kohlenstoffatome enthalten.

5. Verfahren nach Anspruch 1, worin R_4 aus der aus Alkylen, Alkenylen, Arylen, Arylalkylen, Arylalkenylen, Alkyla-
    rylen, Alkenylarylen und Glycolen bestehenden Gruppe ausgewählt ist.

6. Verfahren nach Anspruch 5, worin R_4 ein Alkyl mit acht bis zwanzig Kohlenstoffatomen ist.

7. Verfahren nach Anspruch 6, worin R_4 Oleyl ist.

8. Verfahren nach Anspruch 5, worin R_4 ein Alkenyl mit acht bis 20 Kohlenstoffatomen ist.

9. Verfahren nach Anspruch 5, worin der Rest R_4 ein bis zwanzig Kohlenstoffatome umfaßt.

10. Verfahren nach Anspruch 1, worin die Reste R_4 den Hydratbildungsinhibitor mit einem Polymer verknüpfen.

11. Verfahren nach Anspruch 10, worin das Polymer eine Polyacrylsäure ist.

12. Verfahren nach Anspruch 1, worin R_1, R_2 und R_3 jeweils unabhängig voneinander aus der aus n-Butyl, iso-Pentyl
    und n-Pentyl bestehenden Gruppe ausgewählt sind.

13. Verfahren nach Anspruch 12, worin das Hydratbildungsinhibitorkation aus der aus Tributyldecylammonium, Tri-
    pentyldecylammonium, Tributyloleylammonium, Tributylhexadecylammonium, Tributylhexadecylphosphonium
    und Tributyloleylphosphonium bestehenden Gruppe ausgewählt ist.

14. Verfahren nach Anspruch 1, worin Y aus der aus Hydroxid, Carboxylat, Halogenid, Sulfat und organischem Sulfonat
    bestehenden Gruppe ausgewählt ist.

15. Verfahren nach Anspruch 1, worin die Menge des Hydratbildungsinhibitors zwischen 0,05 und 5 Gew.-%, bezogen
    auf das Wasser im Gemisch, liegt.

16. Verfahren nach Anspruch 15, worin die Menge des Hydratbildungsinhibitors zwischen etwa 0,1 und 0,5 Gew.-%
    des Wassers im Gemisch liegt.

17. Verfahren nach Anspruch 2, worin R_1, R_2 und R_3 jeweils unabhängig aus der aus n-Butyl, iso-Pentyl und n-Pentyl
    bestehenden Gruppe ausgewählt sind.

Revendications

1. Procédé pour inhiber le colmatage ou l'obstruction d'une conduite, laquelle conduite contient un mélange en écoulement comprenant une quantité d'hydrocarbures possédant de un à cinq atomes de carbone et une quantité d'eau, où les quantités d'hydrocarbures et d'eau peuvent former des hydrates aux pressions et températures subies par la conduite, le procédé comprenant les étapes consistant à :

   ajouter au mélange une quantité d'un composant inhibiteur de formation d'hydrate de la formule

$$\left[\begin{array}{c} R_1 \\ | \\ R_3-X \\ | \\ R_2 \end{array} \right]^{+} \quad Y^{-}$$
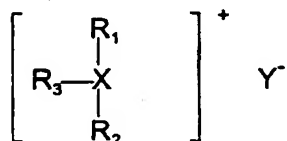
   dans laquelle R_1, R_2 et R_3 sont indépendamment choisis dans le groupe formé par des radicaux alkyle normaux et ramifiés possédant au moins 4 atomes de carbone,
   X est choisi dans le groupe formé par S, N-R_4 et P-R_4,
   R_4 est choisi dans le groupe formé par l'hydrogène et des substituants organiques et
   Y^- est un anion, la quantité efficace pour inhiber la formation d'hydrates dans le mélange aux pressions et températures subies par la conduite et
   faire s'écouler le mélange contenant l'inhibiteur de formation d'hydrate à travers la conduite.

2. Procédé suivant la revendication 1, caractérisé en ce que X est N-R_4.

3. Procédé suivant la revendication 1, caractérisé en ce que X est P-R_4.

4. Procédé suivant la revendication 1, caractérisé en ce que R_1, R_2 et R_3 possèdent chacun de 4 à 6 atomes de carbone.

5. Procédé suivant la revendication 1, caractérisé en ce que l'on choisit R_4 dans le groupe formé par les radicaux alkyle, alcényle, aryle, arylalkyle, arylalcényle, alkylaryle, alcénylaryle et les glycols.

6. Procédé suivant la revendication 5, caractérisé en ce que R_4 représente un radical alkyle possédant de huit à vingt atomes de carbone.

7. Procédé suivant la revendication 6, caractérisé en ce que R_4 représente le radical oléyle.

8. Procédé suivant la revendication 5, caractérisé en ce que R_4 représente un radical alcényle possédant de huit à vingt atomes de carbone.

9. Procédé suivant la revendication 5, caractérisé en ce que R_4 comprend de un à vingt atomes de carbone.

10. Procédé suivant la revendication 1, caractérisé en ce que les radicaux R_4 lient l'inhibiteur de formation d'hydrate à un polymère.

11. Procédé suivant la revendication 10, caractérisé en ce que le polymère est un poly(acide acrylique).

12. Procédé suivant la revendication 1, caractérisé en ce que R_1, R_2 et R_3 sont choisis chacun indépendamment dans le groupe formé par les radicaux n-butyle, isopentyle et n-pentyle.

13. Procédé suivant la revendication 12, caractérisé en ce que le cation inhibiteur de formation d'hydrate est choisi dans le groupe formé par les cations tributyldécylammonium, tripentyldécylammonium, tributyloléylammonium, tributylhexadécylammonium, tributylhexadécylphosphonium et tributyloléylphosphonium.
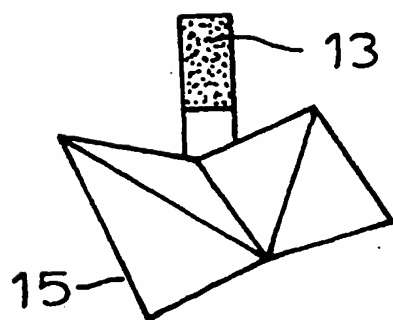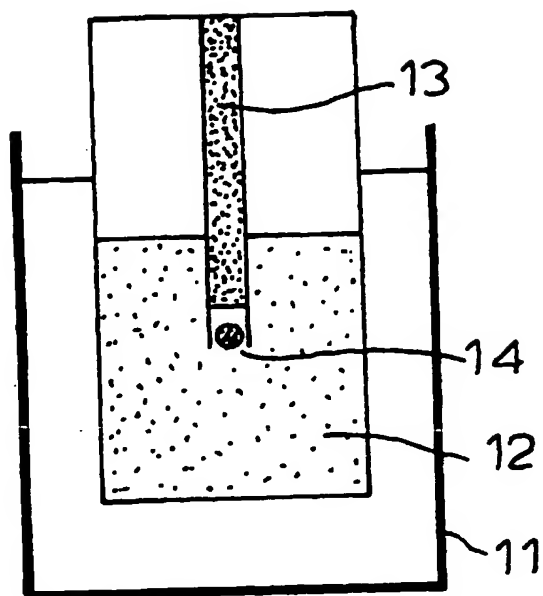
14. Procédé suivant la revendication 1, caractérisé en ce que Y est choisi dans le groupe formé par les hydroxydes, les carboxylates, les halogénures, les sulfates et les sulfonates organiques.

15. Procédé suivant la revendication 1, caractérisé en ce que la quantité d'inhibiteurs de formation d'hydrate varie de 0,05 à 5% en poids, sur base de l'eau dans le mélange.
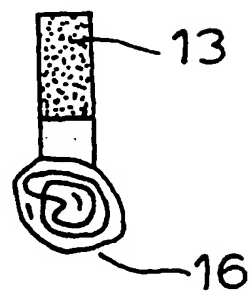
16. Procédé suivant la revendication 15, caractérisé en ce que la quantité de l'inhibiteur de formation d'hydrate varie de 0,1 à 0,5% en poids de l'eau dans le mélange.

17. Procédé suivant la revendication 2, caractérisé en ce que R_1, R_2 et R_3 sont choisis chacun indépendamment dans le groupe formé par les radicaux n-butyle, isopentyle et n-pentyle.
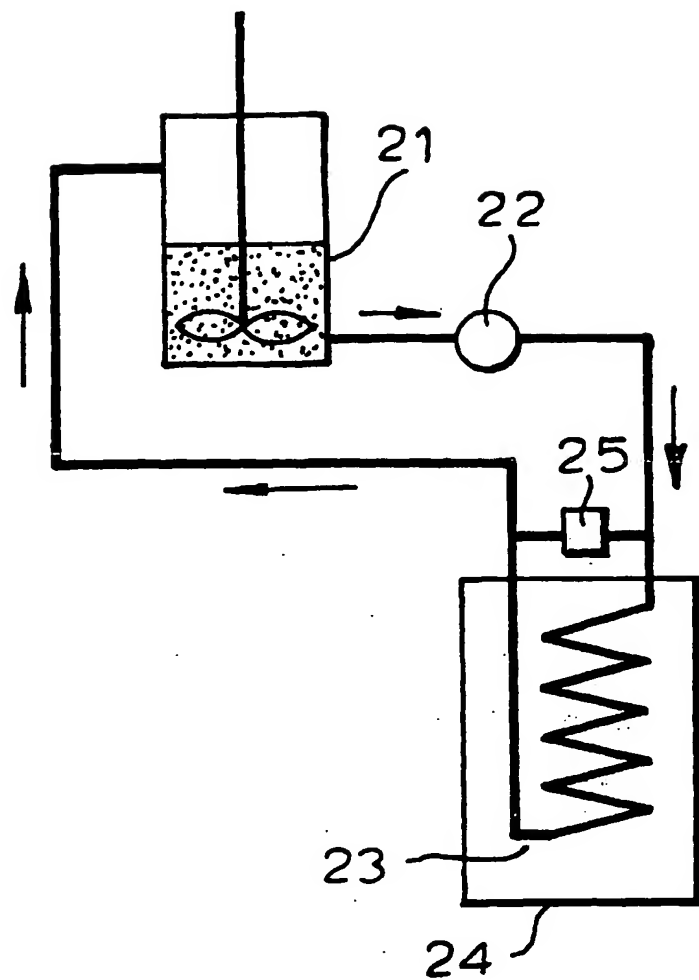
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FIG.1A

FIG. 1B

FIG.1C

FIG.2

FIG.3